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MATHEMATICAL THEORY OF LAMINAR COMBUSTION. I. GOVERNING EQUATIO--ETC(U)

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J. D. Buckmaster and G. S. S. Ludford

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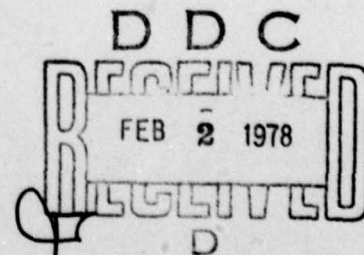
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I. GOVERNING EQUATIONS

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ABSTRACT

The governing equations of combustion are derived from the standpoint of continuum mechanics; and an indication is given of how their rational analysis can be based on activation-energy asymptotics.

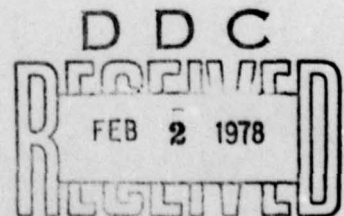
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SIGNIFICANCE AND EXPLANATION

A simple but careful derivation is given of the partial differential equations describing the flow of a chemically reacting mixture. Simplifying assumptions are then made so as to analyse these equations. It is finally shown that the largeness of the so-called activation energy in many combustion processes enables asymptotic methods, very familiar to fluid dynamicists, to be used in their solution.

The responsibility for the wording and views expressed in this descriptive summary lies with MRC, and not with the authors of this report.

MATHEMATICAL THEORY OF LAMINAR COMBUSTION

I. GOVERNING EQUATIONS

J. D. Buckmaster and G. S. S. Ludford

1. Introduction

There are two aspects to the development of the governing equations of combustion: derivation of the equations of a chemically reacting mixture and then judicious simplifications to render these equations tractable while retaining essential characteristics. A rigorous derivation requires a long apprenticeship in either kinetic theory or continuum mechanics. (Indeed, the general continuum theory of reacting mixtures is only just being perfected.) We choose instead the path of a plausible (but potentially rigorous) derivation, guided by experience with a single fluid, through the continuum theory of a mixture of fluids. Such a derivation is not common in the literature, which tends to run to ad hoc argument when it cannot face either of the rigorous ones. In particular, the inconsistent assumption that the mixture itself is a fluid for the purpose of introducing certain constitutive relations will not be made.

The combustion approximation, characterizing it as an essentially isobaric process, is a safe simplification. But the remaining simplifications, designed as they are solely to make the equations tractable, should be accepted tentatively: they are always revocable in the light of faulty predictions. For that reason they should be explained carefully, but are usually not. Nevertheless, whoever is primarily interested in solving non-trivial combustion problems (as we are) can have the same confidence in the final equations as is normally placed in the Navier-Stokes equations.

These final equations retain most of the complexity of a compressible, heat-conducting, viscous fluid but add diffusion of the species and source terms representing the chemical reaction. This complexity has usually been fought with irrational approximation and computers. However, combustion processes, by their very nature, tend to have large

activation energies. It is therefore more natural for a fluid dynamicist to analyze the problem rationally by localizing the reaction, for example, in layers (or flames), which Sec. 8 will show can be done through activation-energy asymptotics. Such an approach was scarcely mentioned before the review article of Williams (1971), which contains the first suggestion of so forming the basis of a mathematical theory of combustion. To be sure, the classic paper of Bush & Fendell (1970) came earlier, but Williams marked the start of a clear path through the complex and fascinating problems of combustion, at least for the present writers.

Our intention then is to arrive as quickly as possible at a convincing set of equations and a method of attack, with which to get on with discussing combustion phenomena.

2. Continuum Approach to a Mixture of Reacting Species

The mixture has density ρ and is considered to be made up of N fluids whose separate densities are ρY_i ($i = 1, 2, \dots, N$). Here the Y_i are mass fractions (or concentrations), with

$$(1) \quad \sum_{i=1}^N Y_i = 1.$$

If v_i is the velocity of the i th fluid (or species), balance of mass requires

$$(2) \quad \partial(\rho Y_i)/\partial t + \nabla \cdot (\rho Y_i v_i) = \dot{\rho}_i,$$

where $\dot{\rho}_i$ is the rate of production of species i (mass per unit volume) by the chemical reactions so that

$$(3) \quad \sum_{i=1}^N \dot{\rho}_i = 0.$$

Summation of the equations over all species therefore yields the familiar continuity equation

$$(4) \quad \partial \rho / \partial t + \nabla \cdot (\rho v) = 0,$$

where

$$(5) \quad v = \sum_{i=1}^N Y_i v_i$$

is the mass-average velocity of the mixture. Each balance equation (2) can now be re-cast by subtracting Y_i times the overall equation (4) and introducing the diffusion velocities

$$(6) \quad v_i = v_i - v;$$

this gives

$$(7) \quad \rho (\partial Y_i / \partial t + v \cdot \nabla Y_i) = \dot{\rho}_i - \nabla \cdot (\rho Y_i v_i).$$

The momentum balances of the separate species will not be written down since they play no role in the sequel. But Truesdell (1965) shows that if they are added the result is the single-fluid balance

$$(8) \quad \rho (\partial v / \partial t + v \cdot \nabla v) = \nabla \cdot \Sigma + \rho g,$$

provided no momentum is created by the chemical reactions. Here Σ is the sum of the

separate stresses plus stresses due to diffusion of the species and \mathbf{q} is the gravity force, assumed to be the only force external to the mixture. Interactions between the species [cf. the discussion of Fick's law (19)], which give additional external forces on each individual species, sum to zero.

We shall also forego writing the energy balances for the separate species, but Truesdell shows their sum gives the single-fluid balance

$$(9) \quad \rho(\partial U / \partial t + \mathbf{v} \cdot \nabla U) = \sum_i \nabla \cdot \mathbf{T}_i + \nabla \cdot \mathbf{q} ,$$

provided no energy is created by the chemical reactions and the work of the interaction forces is negligible. Here U is the sum of the separate internal energies plus kinetic energies of diffusion while \mathbf{q} is the sum of the separate energy fluxes plus fluxes due to diffusion. Note that the work of the gravity force has not been neglected: it is

$$\sum_{i=1}^N (\rho Y_i) \mathbf{g} \cdot \mathbf{v}_i = 0 \text{ by virtue of the result}$$

$$(10) \quad \sum_{i=1}^N Y_i \mathbf{v}_i = 0 ,$$

which follows from the definition (6).

The new variables $\dot{\rho}_i$, \mathbf{v}_i , Σ , U and \mathbf{q} introduced by these balances have to be related to the basic variables by constitutive equations. Continuum mechanics does not supply such relations but rather judges them for consistency with certain general principles after they have been proposed. For reacting mixtures such judgements are still being made, but the linear equations we shall write down are acceptable (Bowen, 1976). With the exceptions of $\dot{\rho}_i$ and \mathbf{v}_i they come from experience with a single fluid. The coefficients (37) which will appear are, for the moment, to be considered functions of the basic variables.

The basic variables will be Y_i , \mathbf{v} , ρ and p ; but in formulating the constitutive equations it is convenient to introduce the temperature T , which is assumed to be the same for all species. If each species is a perfect gas its partial pressure is

$$(11) \quad p_i = R(\rho Y_i) T / m_i ,$$

and the consequence

$$(12) \quad p = R \rho T \sum_{i=1}^N (Y_i / m_i)$$

of Dalton's law determines the common temperature. Here R is the gas constant and m_i is the mass of a molecule of species i . The separate internal energies of the species are then functions of T alone, which may be written

$$(13) \quad U_i = h_i - p_i / (\rho Y_i)$$

where the enthalpies are

$$(14) \quad h_i = h_i^0 + \int_{T^0}^T c_{pi}(T) dT$$

Here h_i^0 is the heat of formation of the species i at some standard temperature T^0 and the c_{pi} are the specific heats at constant pressure. If we neglect kinetic energies of diffusion for being nonlinear in the v_i , the internal energy of the mixture is now

$$(15) \quad U = \sum_{i=1}^N Y_i h_i - p / \rho$$

Next the energy flux q is specified by requiring that the separate energy fluxes be due entirely to heat conduction, so that

$$(16) \quad q = \lambda \nabla T - \rho \sum_{i=1}^N Y_i h_i v_i$$

where λ , the coefficients of thermal conductivity of the mixture, is the sum of the species coefficients. Each of the diffusion fluxes is that of a single fluid moving relative to the mixture with velocity v_i when kinetic energy and deviation of the stress tensor (17) from $-p_i I$ are neglected, the latter anticipating the combustion approximation (Sec. 5) which makes v_i small. Such a q neglects, in particular, radiative transfer and the Dufour effect (heat flux due to concentration gradients).

The separate stresses are assumed to be Newtonian, i.e.

$$(17) \quad \tau_i = -(p_i + 2\kappa_i \nabla \cdot v_i / 3) I + \kappa_i [\nabla v_i + (\nabla v_i)^T]$$

where I is the unit tensor and bulk viscosity has been neglected. We shall take the remaining coefficients $\kappa_i = Y_i \kappa$, which amounts to supposing that the intrinsic viscosities

of the species are all equal. [Otherwise gradients of V_i must be neglected in comparison with those of v to arrive at the result (18).] Since stresses due to diffusion and terms $V_i \nabla V_i$ are nonlinear, these sum to give

$$(18) \quad \underline{\Sigma} = -(p + 2\kappa \nabla \cdot \underline{v} / 3) \underline{I} + \kappa [\underline{\nabla v} + (\underline{\nabla v})^T]$$

by virtue of the result (10).

The thermomechanical constitution is completed by equations for the diffusion velocities V_i ; we adopt Onsager's (1945) generalization

$$(19) \quad \rho Y_{i-1} V_i = - \sum_{j=1}^N \mu_{ij} \nabla Y_j$$

of Fick's (1855) law, making each diffusive mass flux a linear combination of the concentration gradients. Now the condition (1) and the result (10) imply that

$$\sum_{i=1}^N \sum_{j=1}^N \mu_{ij} \nabla Y_j = \sum_{j=1}^{N-1} \left[\sum_{i=1}^N (\mu_{ij} - \mu_{iN}) \right] \nabla Y_j = 0$$

where the remaining gradients are independent of each other. It follows that the coefficients μ_{ij} must satisfy

$$(20) \quad \sum_{i=1}^N \mu_{ij} = \sum_{i=1}^N \mu_{iN} \quad \text{for } j = 1, 2, \dots, N-1.$$

An equivalent of the law (19), in which the gradients are expressed as linear combinations of the diffusion velocities, can be derived from the separate momentum balances by making assumptions about the interaction forces between the species (Williams 1965, p. 416). An implicit new assumption in such arguments is that the accelerations $\partial V_i / \partial t$ are negligible. They only occur in unsteady problems and then produce a finite velocity of propagation of diffusion effects (Müller 1977); as such, they appear to be of no great importance in combustion. The constitutive equation (19) is the only non-chemical one which does not come from experience with a single fluid. Note that the rate of working of these interaction forces is nonlinear in V_i so that we are justified in using equation (9).

Finally we come to the $\dot{\rho}_i$, which require a discussion of chemical reactions.

3. The Arrhenius Factor (1889)

For simplicity we shall first consider one-step combustion, where a single unopposed chemical reaction is involved. If N_i is the number of molecules of species i per unit volume, then (by definition)

$$(21) \quad \dot{\rho}_i = m_i \dot{N}_i.$$

The chemical reaction may be described in terms of the m_i as the mass balance

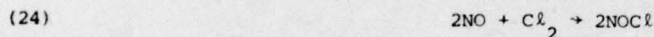
$$(22) \quad \sum_{i=1}^N v_i m_i = \sum_{i=1}^N \lambda_i m_i,$$

where coefficients v_i, λ_i are the stoichiometric integers, each a non-negative integer. v_i is zero if the species i is not a reactant, while λ_i is zero if it is not a product. Both are zero for an inert. Since these coefficients represent the relative numbers of molecules consumed or produced by the reaction we may write

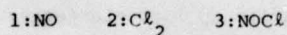
$$(23) \quad \dot{N}_i = (\lambda_i - v_i) \omega,$$

where ω measures the rate at which the reaction is proceeding. Clearly the requirement (3) is now a consequence of the definition (21) and the mass balance (22).

For example, consider the exothermic reaction



by which nitrosyl chloride is formed from nitric oxide and chlorine. If the three species are numbered



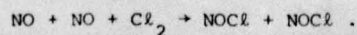
then the stoichiometric integers are

$$v_1 = 2, v_2 = 1, v_3 = 0; \quad \lambda_1 = 0, \lambda_2 = 0, \lambda_3 = 2,$$

and

$$\dot{N}_1 = -2\omega, \dot{N}_2 = -\omega, \dot{N}_3 = 2\omega$$

are the rates of consumption (negative) and production (positive) of molecules. Note that, when single molecules are used, the reaction (24) is written



It is therefore ω which must be related to the basic variables; a common assumption is that it is proportional to the number density (concentration) $\rho Y_j / m_j$ of each reactant, where the species j is counted ν_j times as a reactant [cf. the single-molecule form of the reaction (24)]. Thus

$$(25) \quad \omega = k \prod_{j=1}^N \left(\frac{\rho Y_j}{m_j} \right)^{\nu_j} = k \rho^{\nu} \prod_{j=1}^N \left(\frac{Y_j}{m_j} \right)^{\nu_j} \quad \text{where } \nu = \sum_{j=1}^N \nu_j$$

and the factor k is supposed to depend only on the temperature. (Since experimental determinations of k are done under isothermal conditions, it is called the rate constant; but we shall avoid the term since the temperature dependence of k is an essential feature in our analysis.) The Arrhenius law

$$(26) \quad k = B T^{\alpha} e^{-E/RT}$$

is invariably taken for its variation with temperature, where B , α ($\approx 1/2$ theoretically), E are constants. The latter is known as the activation energy since E/R is roughly the temperature below which k is small. In short, we now have

$$(27) \quad \dot{\rho}_i = \mu_i \omega$$

where

$$(28) \quad \mu_i = m_i (\lambda_i - \nu_i) \quad \text{and} \quad \omega = B T^{\alpha} e^{-E/RT} \rho^{\nu} \prod_{j=1}^N \left(\frac{Y_j}{m_j} \right)^{\nu_j}.$$

More complex reactions are first split up into elementary reaction steps, which may contain reversals of each other (opposing reactions). For each elementary reaction a formula (27) holds and for the complete reaction $\dot{\rho}_i$ is the sum of all such terms. (A pair of opposing reactions may be in equilibrium, i.e. the corresponding terms cancel and thereby furnish an algebraic relation between mass fractions.) The central question of reaction kinetics is to determine these elementary steps and their parameters B , α , E .

In practice a combustion reaction may be a complex network of elementary steps. Attempts are therefore made to model the overall reaction with a smaller number of terms of the form (27), preferably one. The exponents ν_i are then released from being the

stoichiometric coefficients of the overall reaction and ν is not necessarily their sum. On the other hand, the ν_i retain their meaning since they still represent the proportions in which the species take part in the reaction. The free constants B , α , E , ν , ν_i are determined experimentally; of course the ν_i need no longer be integers.

4. Differential Diffusion. Equality of Specific Heats and of Molecular Masses

Once the various parameters (constants and functions) which appear in the constitutive equations (12), (15), (16), (18), (19), (27) are given, there are $N + 6$ equations (1), (4), (7), (8), (9) for the $N + 5$ unknowns Y_i , v , ρ , p . Equation (1) is consistent with the remainder since they conserve $\sum_{i=1}^N Y_i$ whenever the relations (20) hold between the ν_{ij} ; initial or boundary conditions will then give it the value 1. The system is clearly very complicated as it stands, and must be simplified if it is to yield to detailed analysis.

The law (19) leads to terms

$$(29) \quad \sum_{j=1}^N \nabla \cdot (\nu_{ij} \nabla Y_j)$$

in the mass balances (7). To simplify these terms while retaining different diffusion properties for the species, it is tempting to set

$$(30) \quad \nu_{ij} = 0 \quad \text{for } i \neq j$$

and allow the ν_{ii} to change with i (Emmons 1971). However the conditions (20) would be violated: they require

$$(31) \quad \nu_{ii} = \nu_{NN} = \nu(\text{say}) \quad \text{for all } i.$$

The conclusions (30) and (31) are reached quite generally by Williams' theory when the so-called binary diffusion coefficients are equal, i.e. whenever the interactions between pairs of species are identical so far as momentum is concerned.

However, effectively the same goal can be reached by taking the values (30) for all i except the last, and

$$(32) \quad \nu_{Nj} = \nu_{NN} - \nu_{jj} \quad \text{for } j \neq N$$

with the ν_{jj} different. The conditions (20) are now satisfied and the terms (29) simplify to

$$(33) \quad \nabla \cdot (\nu_{ii} \nabla Y_i) \quad \text{for } i \neq N.$$

Only the N th equation remains complicated but, since Y_N can be otherwise calculated from $1 - \sum_{i=1}^{N-1} Y_i$, that does not matter. Such a scheme can be justified from Williams'

formulas when the first $N-1$ species are scarce compared to the last, an extreme often met in combustion where, for example, reactants are diluted in an inert species so as to prevent explosions.

In short, we shall generally take the values (30) and (31) but, when differential diffusion cannot be ignored, the μ_{ii} ($i = 1, 2, \dots, N-1$) will be given different values. The results will then apply to a mixture of reactants and products highly diluted in an inert. Note that a common value of the μ_{ii} can still depend on the Y_i and, in particular, be a different constant when different Y_i vanish. Such is the case in the burning of a fuel droplet treated by Kassoy & Williams (1968). They use different diffusion coefficients for the fuel and oxidant equations but do not apply the equations in the same place: the combustion field is divided into two parts, in each of which there is either no fuel or no oxidizer. There is no question of an abundant inert.

We come now to the energy balance (9). First note that the individual c_{pi} disappear from U in favor of

$$(34) \quad c_p(T, Y_i) = \sum_{i=1}^N Y_i c_{pi}.$$

Thus we have immediately

$$(35) \quad U = \sum_{i=1}^N Y_i h_i^0 + I - p/\rho$$

where

$$(36) \quad I(T, Y_i) = \sum_{i=1}^N Y_i \int_{T^0}^T c_{pi} dT = \int_{T^0}^T c_p dT,$$

the last integral being taken with the Y_i fixed, i.e. for constant composition. Adoption of $\mu_{ij} = \mu \delta_{ij}$ ensures that the same happens to q : we have

$$(37) \quad \begin{aligned} \rho \sum_{i=1}^N Y_i h_i V_i &= \rho \sum_{i=1}^N Y_i h_i^0 V_i - \mu \sum_{i=1}^N \left(\int_{T^0}^T c_{pi} dT \right) \nabla Y_i \\ &= \rho \sum_{i=1}^N Y_i h_i^0 V_i - \mu \left(\nabla I - \sum_{i=1}^N Y_i c_{pi} \nabla T \right) \\ &= \rho \sum_{i=1}^N Y_i h_i^0 V_i + \mu (c_p \nabla T - \nabla I). \end{aligned}$$

Next note the form which the energy balance now takes. The total contribution to the equation from the heats of formation h_i^0 , when placed on the right-hand side, is

$$(38) \quad - \sum_{i=1}^N h_i^0 [\rho (\partial Y_i / \partial t - \mathbf{v} \cdot \nabla Y_i) + \nabla \cdot (\rho Y_i \mathbf{v}_i)] = - \sum_{i=1}^N h_i^0 \dot{b}_i$$

according to the mass balances (7). Also the total contribution from heat conduction and terms containing c_p , when placed on the left-hand side, is

$$(39) \quad \rho (\partial I / \partial t + \mathbf{v} \cdot \nabla I) + \nabla \cdot [\mu (c_p \nabla T - \nabla I) - \lambda \nabla T]$$

The remaining terms, when placed on the right-hand side, contribute

$$(40) \quad \partial p / \partial t + \mathbf{v} \cdot \nabla p - 2\kappa (\nabla \cdot \mathbf{v})^2 / 3 + \kappa [\nabla \mathbf{v} + (\nabla \mathbf{v})^T] : \nabla \mathbf{v}$$

according to the continuity equation (4). In the combustion approximation discussed later the velocity is small, implying also that the pressure is effectively a spatial constant, so that these last terms are ignored except for $\partial p / \partial t$, which is a function of t alone.

It is tempting to take the Lewis number

$$(41) \quad L = \lambda / \mu c_p$$

equal to 1; then the terms (39) contain I only. However, if the c_{pi} are not all equal, c_p is a linear function (34) of the Y_i which μ/λ can only equal for very special mixtures (if at all). Only when the c_{pi} are all equal does c_p lose its dependence on the composition of the mixture, and then it is unnecessary to make any assumption about the Lewis number as we shall see next.

We are therefore faced with taking all the c_{pi} equal, when c_p becomes a function of T alone:

$$(42) \quad c_p(T) = c_{pi} \quad \text{for all } i.$$

Since ∇I is then $c_p \nabla T$ the energy equation reads

$$(43) \quad \rho (\partial I / \partial t + \mathbf{v} \cdot \nabla I) - \nabla \cdot [(\lambda / c_p) \nabla I] = - \left[\sum_{i=1}^N h_i^0 \mu_i \right] \omega + \partial p / \partial t$$

where

$$(44) \quad I(T) = \int_{T^0}^T c_p dT$$

is a function of T only and we have used (27). So far as specific enthalpy is concerned the species are distinguished only by their heats of formation; thus equation (43) is that of a single fluid in which differences in these heats are liberated as reactants change into products. [It should be noted that the same equation results under the assumption of equal specific heats even when there is differential diffusion.] The species equations (7) take a similar form

$$(45) \quad \rho (\partial Y_i / \partial t + \mathbf{v} \cdot \nabla Y_i) - \nabla \cdot (\rho \nabla Y_i) = \nu_i \omega$$

Another complication is the presence of the mass fractions in the equation of state (12). They effectively disappear if the first $N-1$ species are scarce compared to the last; but the same simplification can only be achieved in general when all the molecular masses are the same, i.e.

$$(46) \quad m_i = m \text{ (say) for all } i$$

Then the law (12) becomes

$$(47) \quad p = \rho R T / m$$

so that the mixture behaves like a perfect gas. Such is the case when the reaction changes a single molecule into a single molecule, but otherwise the condition is never met exactly in practice.

We may expect our equations to govern the behavior of a mixture for which c_{pi} and m_i do not vary much from species to species. In practice c_p and m would be given intermediate values, e.g. $\sum_{i=1}^N Y_i c_{pi}$ and $\left[\sum_{i=1}^N Y_i / m_i \right]^{-1}$ for a characteristic set of Y_i . More serious is the consequence (31) of the assumption (30). Differential diffusion is known to be responsible for important effects in biological systems, in particular pattern formation (Othmer 1977); and is believed to produce instability leading to the cellular structure of flames (Markstein 1964, p. 75). Luckily the latter question can be tackled with the alternatives (32) and (33). Either there is an abundant inert or all but the single product species (substituting for the inert) are scarce near the flame, whose vicinity alone need be considered.

The coefficients

(48)

$$\kappa, \lambda, \mu, c_p$$

are functions of the basic variables Y_1, ρ and p . Further simplifications will result from taking them constant, but we shall delay writing down the equations until those are made dimensionless later.

5. The Combustion Approximation and Its Constant-Density Approximation

While the simplifications introduced so far have the nature of idealizations which are approached more or less by actual mixtures, the basic approximation of the theory characterizes combustion as a low-speed phenomenon in a chemically reacting compressible mixture for which gravity is unimportant. More precisely, the kinetic energy is small compared to the thermal energy so that a representative Mach number is small.

An immediate consequence is that spatial variations in pressure are also small, so that we may set

$$(49) \quad p = p_c(t)$$

everywhere except in the momentum equation (8). [The notation indicates that the pressure can be controlled, for example in the surroundings.] This conclusion is reached from the momentum equation, which shows that fractional changes in pressure at any time are proportional to the Mach number (both through $\partial v/\partial t$ and the viscous terms). The pressure can still vary in time, but a subsidiary feature of the combustion approximation is that, when it does, the variations are small ones about some constant value \bar{p}_c .

Buoyancy would appear to be an important factor in certain combustion problems. If so, ρg should be retained in the momentum equation and the conclusion (49) cannot be drawn. Such a problem is the burning of a fuel drop but, nevertheless, remarkably accurate predictions of combustion characteristics, as opposed to the flow field (which is not of primary interest), result from neglect of gravity. [Cf. Williams (1965, p. 48).] The reason may lie in the absence of gravity from the energy equation (9) and in an overall insensitivity of its solutions to inaccurate determinations of the convection ρv .

It is tempting to think that the momentum equation can now be discarded because its only role is the calculation of these small "flow-induced" variations in pressure. But that would leave $N + 2$ equations for the $N + 4$ unknowns Y_i, v, ρ . If these variations must be eliminated, the momentum equation should be replaced by its own curl (Helmholtz equation), which provides two independent scalar equations. We prefer to leave it intact and interpret p as the small, flow-induced variation in pressure from its value p_c .

If the reaction rate ω is zero (as it is in whole regions for the asymptotic approach we shall describe in Sec. 8), the five equations (4), (8), (43) for the five unknowns v , p , ρ become uncoupled from the species equations. They can be recognized as the equations of motion of a viscous, heat-conducting, compressible fluid, for which few exact solutions are known. To be sure, the combustion approximation has been applied but such modification leaves them only slightly more tractable. A non-zero ω can only make analytical solution more difficult, which accounts for the heavy reliance on numerical methods in the combustion literature.

Most progress can be made for steady conditions, since only the mass flux ρv is needed to make the energy equation (43) and species equations (45) a determinate set for T and Y_i . For certain geometries the mass flux is obvious a priori while for others it can be approximated locally. The most important example of the former is a uniform flux in the x -direction, for which

$$(50) \quad \rho v = M_i, M \text{ const.}$$

It can be used when T varies with x alone, but otherwise needs justification. If T also varies radially from the x -axis, then so do $\rho = p_c m/RT$ and the velocity. While there are such unidirectional velocity fields satisfying the momentum equation these are not amongst them (as is easily shown). Burke & Schumann (1928), in tackling what may be regarded as the first combustion problem, ignored this inconsistency.

Justification comes when the variations in temperature are due entirely to the combustion and the heat release is small compared to the thermal energy of the mixture. Since the density variations are correspondingly small, the velocity field is that of a constant-density fluid to leading order. The undisturbed values of ρ and ρv may be used in equations (43) and (45) to determine the leading terms in the mass fractions and the perturbation of the temperature. In short, Burke & Schumann introduced the constant-density approximation, a rational scheme valid even for unsteady problems. No attempt has been made to take it any further than they did.

6. Constant Properties. Dimensionless Variables.

The coefficients (48) will now be taken constant.

The starting point for making the variables dimensionless is the unit of temperature, which comes from the factor

$$(51) \quad - \sum_{i=1}^N h_{i,i}^0 = m \sum_{i=1}^N h_{i,i}^0 (v_i - \lambda_i) = \nu m Q \text{ (say)}$$

on the right-hand side of the energy equation (43). Q is the excess of the total heat of formation of the reactants over that of the products per unit mass of the reactants (or products), i.e. the heat per unit mass released by the reaction at the standard temperature T^0 . [When all the $c_{pi}(T)$ are equal, as here, it is also the heat released at any temperature.] Combustion is only concerned with exothermic reactions such as (24) and then $Q(>0)$ is called the (specific) heat of combustion. The unit of temperature is taken to be Q/c_p , so that the perfect gas law becomes

$$(52) \quad T = p_c / \rho$$

if pressure is referred to \bar{p}_c and density to $\rho_c = c_p \bar{p}_c m / QR$.

The pressure \bar{p}_c will be varied from 0 to ∞ , so that the choice of density unit ensures that ρ stays finite. The same should hold for the mass flux but there is no such combination of existing parameters (excluding the inappropriate rate constant B). We therefore take a representative mass flux M and refer the velocity to M/ρ_c . A diffusion length $\lambda/c_p M$ and a diffusion time $\rho_c \lambda/c_p M^2$ can then be defined as units, in recognition that these are the scales for spreading the heat generated by the combustion. Finally pressure variations are referred to M^2/ρ_c .

In these units the governing equations become

$$(53) \quad \partial \rho / \partial t + \nabla \cdot (\rho \mathbf{v}) = 0 ,$$

$$(54) \quad \rho (\partial Y_i / \partial t + \mathbf{v} \cdot \nabla Y_i) - L^{-1} \nabla^2 Y_i = \alpha_i \Omega ,$$

$$(55) \quad \rho (\partial \mathbf{v} / \partial t + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla p + P [\nabla^2 \mathbf{v} + \nabla (\nabla \cdot \mathbf{v}) / 3] ,$$

$$(56) \quad \rho (\partial T / \partial t + \mathbf{v} \cdot \nabla T) - \nabla^2 T = \Omega + \beta \partial p_c / \partial t$$

where the dimensionless rate of heat release per unit volume is

$$(57) \quad \Omega = \Lambda e^{-\theta/T} \prod_{j=1}^N \gamma_j^{\nu_j}, \quad \Lambda = DM^{-2}.$$

Here $P = c_p \kappa / \lambda$ is the Prandtl number, L has the definition (41), the quantities characterizing the chemical reaction are

$$(58) \quad \alpha_i = \nu_i / \nu_m = (\lambda_i - \nu_i) / \nu, \quad \theta = E c_p / Q R,$$

$$(59) \quad D(T) = (B \nu m^{1-\nu} \lambda_Q^{\alpha-\nu} c_p^{\nu-\alpha-1} R^{-\nu-\nu} p_c^{\alpha \nu}) T^{\alpha \nu},$$

and $\beta = (\gamma-1)/\gamma$ where $\gamma = 1/(1-m c_p/R)$ is the ratio of specific heats.

When the geometry provides a characteristic length a the nondimensionalization is usually done differently. $\lambda/\rho_c c_p a$, $\rho_c c_p a^2/\lambda$ and $\lambda^2/\rho_c c_p a^2$ are taken as units of velocity, time and pressure variation, respectively, to give the same equations (53-56) except that now M is missing from the definition (57) of Ω and

$$(60) \quad D(T) = (B \nu m^{1-\nu} \lambda_Q^{\alpha-\nu} c_p^{\nu-\alpha+1} R^{-\nu} a^{2-\nu} p_c^{\alpha \nu}) T^{\alpha \nu}.$$

In effect M has been replaced by the new unit of mass flux $\lambda/c_p a$.

For any species which is solely a reactant/product α_i is negative/positive; also

$$(61) \quad \sum_{i=1}^N \alpha_i = 0,$$

since the ν_i sum to zero according to the mass balance (22). The variations in $D(T)$ are unimportant and its value at some intermediate temperature may be taken; in our analysis only its value at the flame sheet will appear. D may then be called the Damköhler number, representing the pressure p_c . Finally, θ is the dimensionless activation energy.

When the reactants and products are distinct, so that we may take

$$(62) \quad \begin{cases} \lambda_i = 0, \nu_i \neq 0 & \text{for } i = 1, 2, \dots, n \text{ (say)}, \\ \nu_i = 0 & \text{for } i = n+1, n+2, \dots, N, \end{cases}$$

the equations for the products and inerts can be solved after the rest. Thus the first n of the species equations (54) contain only the reactant mass fractions, as does the energy equation (56); together with the equations of continuity (53) and momentum (55) they form

$n + 5$ equations for the $n + 5$ unknowns $Y_1, Y_2, \dots, Y_n, v, \rho$ and p . The coefficients on the right-hand sides of these reactant equations have the property

$$(63) \quad \sum_{i=1}^n \alpha_i = - \sum_{i=1}^n v_i/v = -1.$$

Finally we mention the modifications when differential diffusion is considered: the inert species equation $i = N$ is dropped in favor of $Y_N = 1 - \sum_{i=1}^{N-1} Y_i$ and L is allowed to vary among the remaining species.

7. Shvab-Zeldovich Variables

When the Lewis number (41) is 1, the convection-diffusion operators on the left-hand sides of equations (54,56) are identical, so that

$$(64) \quad (\rho \partial / \partial t + \rho \mathbf{v} \cdot \nabla - \nabla^2) (Y_i - \alpha_i T) = 0 \quad \text{for all } i.$$

The reaction terms have been eliminated to show that the Shvab-Zeldovich variables

$$(65) \quad \tilde{Y}_i = Y_i - \alpha_i T$$

and purely convected and diffused as in an inert mixture. The \tilde{Y}_i can often be determined first, leaving only the temperature equation (56), with the Y_i replaced by $\tilde{Y}_i + \alpha_i T$ in Ω , to be solved. There is therefore considerable advantage in setting

$$(66) \quad L = 1.$$

However, that is not the reason for taking the value (66). The asymptotics of large activation energy require Ω to be zero everywhere except in certain flame sheets, so that there are only convection-diffusion equations to solve there anyway. Inside the flames the convection terms are negligible and the operators are once more identical (except for the factor L^{-1}): local Shvab-Zeldovich variables can be formed for arbitrary Lewis number. The excuse for the value (66) is solely to eliminate an awkward symbol and, whenever significantly different phenomena can be obtained (as in unsteady problems), a general value should be adopted.

These convection-diffusion equations have a particularly simple form when conditions are steady. If the (dimensionless) energy flux

$$(67) \quad \mathbf{E} = \rho T \mathbf{v} - \nabla T$$

is introduced, then

$$(68) \quad \nabla \cdot \mathbf{E} = 0$$

in view of the continuity equation (53). Similarly the (dimensionless) species fluxes

$$(69) \quad \mathbf{J}_i = \rho Y_i \mathbf{v} = \rho Y_i (\mathbf{v} + \mathbf{V}_i) = \rho \mathbf{v} Y_i - L^{-1} \nabla Y_i$$

satisfy

$$(70) \quad \nabla \cdot \mathbf{J}_i = 0.$$

Equation (68) even holds when conditions are unsteady, provided p_c is constant, by virtue of equation (52). (Of course these are nothing more than conservation equations.)

In one dimension, integration is immediate; and, even when reaction is present, the species fluxes are useful as intermediate variables.

8. Activation-Energy Asymptotics

The reaction (24) has an activation temperature E/R of about $2,500^\circ\text{K}$ for the temperature range $273\text{--}523^\circ\text{K}$ (Konrat'ev 1972) so that $\exp(-\theta/T)$ is at most 8×10^{-3} . To be sure, the reaction is exceptional in that stoichiometric integers ν_i are nearly always 0 or 1 and sum to at most 2 (corresponding to unimolecular or bimolecular rather than termolecular reactions); it was chosen to exhibit the square of a concentration in ω . But it is not exceptional in having a relatively large activation temperature; the limit $\theta \rightarrow \infty$ is particularly appropriate for many combustion reactions.

To see an immediate effect of letting $\theta \rightarrow \infty$ it is convenient to write the reaction term (57) in the form

$$(71) \quad \Omega = \Lambda' Y_1^{\nu_1} Y_2^{\nu_2} \dots Y_N^{\nu_N} \exp \theta(1/T_* - 1/T), \quad \Lambda' = \Lambda \exp(-\theta/T_*)$$

where T_* is a characteristic temperature, as yet unspecified. [It will be the temperature of the flame sheet to which the chemical reaction is confined in the limit.] We now assume Λ' is at most algebraically large in θ , i.e. that all the exponential growth of Λ has been removed by the factor $\exp(-\theta/T_*)$. The assumption is justified if, for example, it leads to a consistent determination of D as a function of the burning rate M , which is fixed as θ increases.

Two possibilities now arise. The frozen limit is obtained wherever all reactants are present but T is smaller than T_* . The term Ω is exponentially small so that to all orders in $1/\theta$ there is negligible reaction. The equilibrium limit obtains wherever T is larger than T_* . Thus

$$(72) \quad Y_i = 0 \text{ for some } i,$$

to all orders in $1/\theta$, since otherwise Ω would be exponentially large. Again there is negligible reaction, but now because one of the reactants has been used up. Of course the remaining reactants are still available and they behave as if the chemistry were frozen.

Only where T is approximately equal to T_* , more precisely where $T - T_* = O(\theta^{-1})$, does Ω contribute; so that the reaction is confined to thin regions, known as flame sheets,

and T_* is now identified as the flame temperature. On either side the reaction may be frozen or there may be equilibrium. If the reaction is frozen on both sides of the flame sheet, the combustion is not complete.

It is the flame sheet which determines $\Lambda'(T_*)$ [and hence $D(T_*)$ as a function of M]; for each M there is just one \bar{p}_c giving a structure which can be matched to the limit states on either side. Note how the temperature dependence of D has dropped out: it is treated as a constant in the analysis. The general procedure in any particular problem is now clear. The combustion field is divided into two parts by a flame sheet and either equilibrium or frozen reaction is assigned in each. [The appropriate assignment is rarely obvious in advance, so that the consequences of all possible combinations must usually be worked out.] The two states are then determined as far as possible, their final determination being a result of matching with the structure of the flame sheet. Different structures are obtained for equilibrium on both sides, one side or neither. In certain circumstances the flame may be at a boundary (including infinity). Then there is only one state to be determined and new structures arise.

There are other possibilities for the asymptotics. M and D may both be given and some other parameter is to be determined; then D' may be exponentially large. Slow variations of otherwise steady states (determined as above) can occur on a time scale $O(\theta)$. In so-called thermal runaway the time scale may even be exponential in θ .

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⑨ Technical summary rept.

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